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PROPERTY CHANGES IN GRAPHITE IRRADIATED AT CHANGING IRRADIATION TEMPERATURE

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R. J. PRICE (General Atomic Company)
G. HAAG (Kernforschungsanlage, Jülich GmbH)

Prepared under the Umbrella Agreement for Cooperation in Gas-Cooled Reactor Development between the United States and the Federal Republic of Germany.

Work supported in part by
Contract DE-AT03-76ET35300
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JULY 1979

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed copy $4.50; Microfiche $3.00

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GENERAL ATOMIC PROJECT 6400

JULY 1979

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FIGURES (cont.)

FIGURES (cont.)

ABSTRACT

Design data for irradiated graphite are usually presented as families of isothermal curves showing the change in physical property as a function of fast neutron fluence. In this report, procedures for combining isothermal curves to predict behavior under changing irradiation temperatures are compared with experimental data on irradiation-induced changes in dimensions, Young's modulus, thermal conductivity, and thermal expansivity. The suggested procedure fits the data quite well and is physically realistic.

1. INTRODUCTION

Standard irradiation tests for obtaining design data on graphite are carried out as nearly as possible at a constant temperature, and the test data are presented as families of isothermal plots showing the change in property as a function of fast neutron fluence. Such isothermal test data can be applied directly to the fuel element blocks in a base load HTGR, but in other systems graphite may be irradiated at widely varying temperatures. Large thermal fluctuations would occur in the fuel elements of a pebble-bed HTR utilizing the OTTO cycle, a prismatic block HTGR operating with axial push-through, or a fission-fusion hybrid power system using a breed-burn cycle.

Changing irradiation temperature presents a problem to designers who must choose a method for combining isothermal design plots to predict the property changes accurately. In this report, possible approaches to the problem are outlined, and experimental data obtained from Kernforschungsanlage Jülich, General Atomic Company, and the literature are reviewed. A method for predicting property changes in graphite irradiated at changing temperature is suggested.

2. PROPERTY CHANGES IN ISOTHERMALLY IRRADIATED GRAPHITE

When well-crystallized graphite is irradiated with fast neutrons, interstitials and vacancies are created which coalesce into clusters of various shapes and sizes within the crystallites. These clusters change the dimensions and intrinsic physical properties of the crystallites. In addition, these crystallite dimensional changes cause interactions between the crystallites. This may alter the internal stress pattern and the porosity of the polycrystalline aggregate. The final effect on the bulk properties is due to a combination of property changes within the crystallites and interactions between the crystallites.

2.1. TRANSIENT IRRADIATION-INDUCED PROPERTY CHANGES

Irradiation-induced changes in some properties (for example, thermal conductivity) are dominated by small defect clusters within the crystallites. Such clusters rapidly build up to an equilibrium concentration which depends on the irradiation temperature. As a result, irradiation reduces the thermal conductivity of graphite to a saturation level which decreases with increasing irradiation temperature. This type of property change is transient in the sense that it is easily annealed out at temperatures above the irradiation temperature.

2.2. IRRADIATION-INDUCED DIMENSIONAL CHANGES

Irradiation-induced dimensional changes in graphite are more complex. At irradiation temperatures below about 300°C, the dimensional changes are controlled by small defect clusters within the crystallites and, like the changes in thermal conductivity, they are easily annealed either by post-irradiation heating or by irradiation at a higher temperature (Ref. 1). In contrast, dimensional changes created by irradiation at higher temperatures are produced by a combination of large defect clusters within the crystallites and inter-crystalline interactions. These high temperature dimensional changes are difficult to anneal out and may be described as non-annealable or cumulative, in contrast to the annealable or transient property changes described above.

2.3. OTHER IRRADIATION-INDUCED CHANGES

The changes in other properties, such as Young's modulus and thermal expansivity, are produced by a combination of within-crystallite and inter-crystallite changes. A multiplicity of mechanisms is responsible for the complexity of the irradiation behavior of graphites. In most cases, the isothermal curves which depict property values as functions of neutron fluence do not have simple mathematical forms, and different isotherms do not have the same shape. The curves can be expressed mathematically only as complicated empirical or semi-empirical equations which include temperature and fluence.

The complexity of the damage mechanisms and the property change curves complicates the problem of formulating rules for combining isotherms to predict behavior under changing temperatures. This problem is discussed in the next section.

3. RULES FOR COMBINING ISOTHERMAL CURVES

Simple empirical procedures have been suggested in the literature (Refs. 2 through 4) for transposing isothermal dimensional change curves. Cords and Zimmermann (Ref. 5) have described a semi-empirical model in which irradiation-induced property changes are described by combinations of rate processes and switch functions. While this model has the potential for constructing property change curves for varying temperatures, detailed procedures have not been developed.

The schematic plots in Fig. 1 illustrate three alternative empirical rules to account for the dimensional changes in a typical nuclear graphite irradiated first at 600°C, then at 1000°C. Figure 1(A) shows complete isothermal dimensional change-versus-fluence plots for 600°C and 1000°C. Figures 1(B), (C), and (D) show three alternative ways of joining the 1000°C isotherm to the 600°C isotherm following a step change in temperature to 1000°C after a period of exposure at 600°C.

3.1. RULE 1 - VERTICAL TRANSPOSITION AT EQUAL FLUENCE

Vertical transposition at equal fluence is the simplest of the three procedures, see Fig. 1(B). At the point of temperature change, vertically shift the 1000°C isotherm by an amount $(y_2 - y_1)$ to join the 600°C isotherm at the same fluence. Point A corresponds to point (x_1, y_2) on the isotherm, see Fig. 1(A). No theoretical justification has been proposed for rule 1.

3.2. RULE 2 - HORIZONTAL TRANSPOSITION AT EQUAL PROPERTY VALUE

Rule 2, horizontal transposition at equal property value, is illustrated in Fig. 1(C). At the temperature change point, the 1000°C isotherm is shifted horizontally a distance (x_1 - x_2) to join the 600°C isotherm for the same dimensional change value. In this case, point A corresponds to point (x_2, y_1) on the isotherm. Rule 2 has some justification when applied to cumulative-type properties, such as high temperature dimensional change, if it is assumed that a given dimensional change corresponds to a given state of irradiation damage. The main drawback of rule 2 is that the procedure is sometimes mathematically impossible, as would be the case if the temperature change occurred near the minimum in the 600°C isotherm.

3.3. RULE 3 - HORIZONTAL TRANSPOSITION AT A SCALED FLUENCE

Rule 3 is proposed here as a method which fits the fullest range of properties and fluence situations. It may be described as horizontal transposition at a scaled fluence.

Although different dimensional change isotherms do not have identical shapes, all eventually cross the zero dimensional change line. The fluence where this happens (x_3 and x_4) [see Fig. 1(A)] can conveniently be regarded as defining the "usable lifetime" of the graphite at a given temperature. This makes it possible to define the "scaled fluence" as the actual fluence, γ, divided by the lifetime fluence, L(T). The scaled fluence, $\gamma(T)/L(T)$, characterizes the fraction of the graphite lifetime which has been used up at temperature T. The usable lifetime of a graphite component can then be predicted from a "cumulative damage rule." The graphite reaches the end of its life when:

$$\sum \frac{\gamma(T)}{L(T)} = 1. \qquad (1)$$

Figure 1(D) illustrates the application of the scaled fluence concept to the present problem. The 1000°C isotherm is shifted horizontally until point A (corresponding to a fluence of $x_1 \cdot x_3/x_4$ on the original isotherm) falls at a fluence of x_1. At this point the scaled fluence at 600°C equals the scaled fluence at 1000°C.

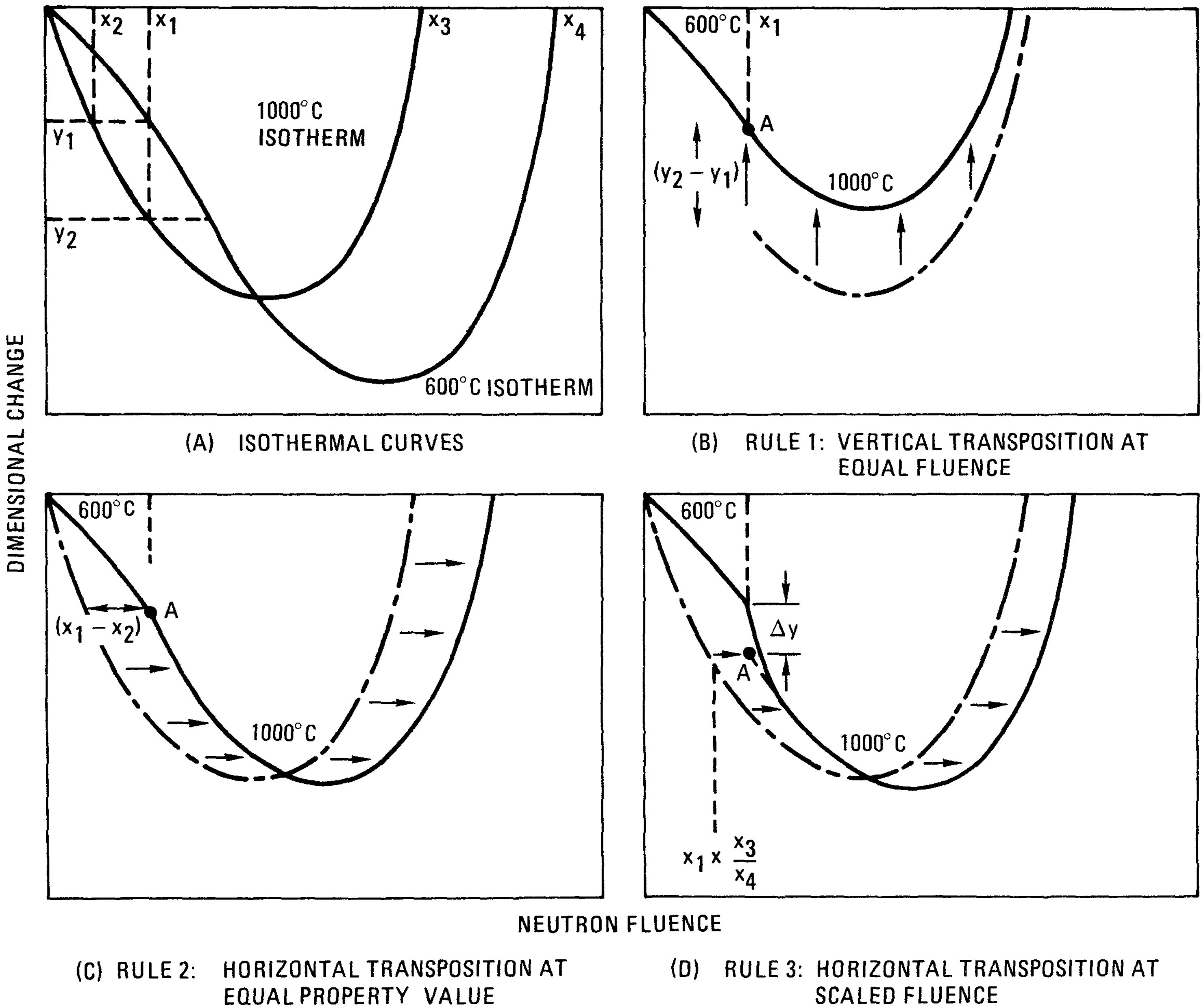

Fig. 1. Alternative rules for transposing isothermal plots of graphite dimensional change versus fluence

However, this procedure usually leaves a gap of Δy between the two isotherms. This gap is assumed to be progressively reduced according to this expression:

$$y = y^* + \Delta y \exp\left(-\frac{\gamma}{\tau}\right) \quad , \tag{2}$$

where y is the predicted property value, y* is the property on the transposed 1000°C isotherm, γ is the fluence measured from the temperature change point, and τ is a time constant.

The progressive approach to the new isotherm is physically reasonable for "transient" properties such as the thermal conductivity, where following a temperature cahnge, the concentration of irradiation-induced defect clusters is expected to move toward the dynamic equilibrium concentration characteristic of the new irradiation temperature. The time constant, τ, in Eq. 2 is taken to be equal to 1×10^{21} n/cm^2, equivalent fission fluence for graphite damage. This value appears to fit the available data reviewed in the following section. For simplicity, it is assumed that lifetime L(T) and time constant τ are the same for all properties and for all near-isotropic graphites. A plot of L(T) versus irradiation temperature is shown in Fig. 2. This plot is derived from the dimensional crossover point for radial specimens of H-451 graphite irradiated at high temperatures, combined with UKAEA data on near-isotropic graphites irradiated at low temperatures (Ref. 6).

The application of the three different transposition rules to changes in dimensions, thermal conductivity, and Young's modulus of a typical near-isotropic graphite is illustrated in Figs. 3 and 4 for a temperature increase and temperature decrease, respectively. In the case of dimensional changes there is not much difference in the behavior predicted by the three rules, except that rule 2 yields no solution when the temperature is stepped up. For thermal conductivity changes, the same situation occurs. In addition, rule 1 predicts no change in conductivity following either an increase or a decrease in temperature. However, this disagrees with observations reported in the next section. For Young's modulus changes, only rule 3 predicts both a decrease in modulus when the temperature rises and an increase when the temperature drops.

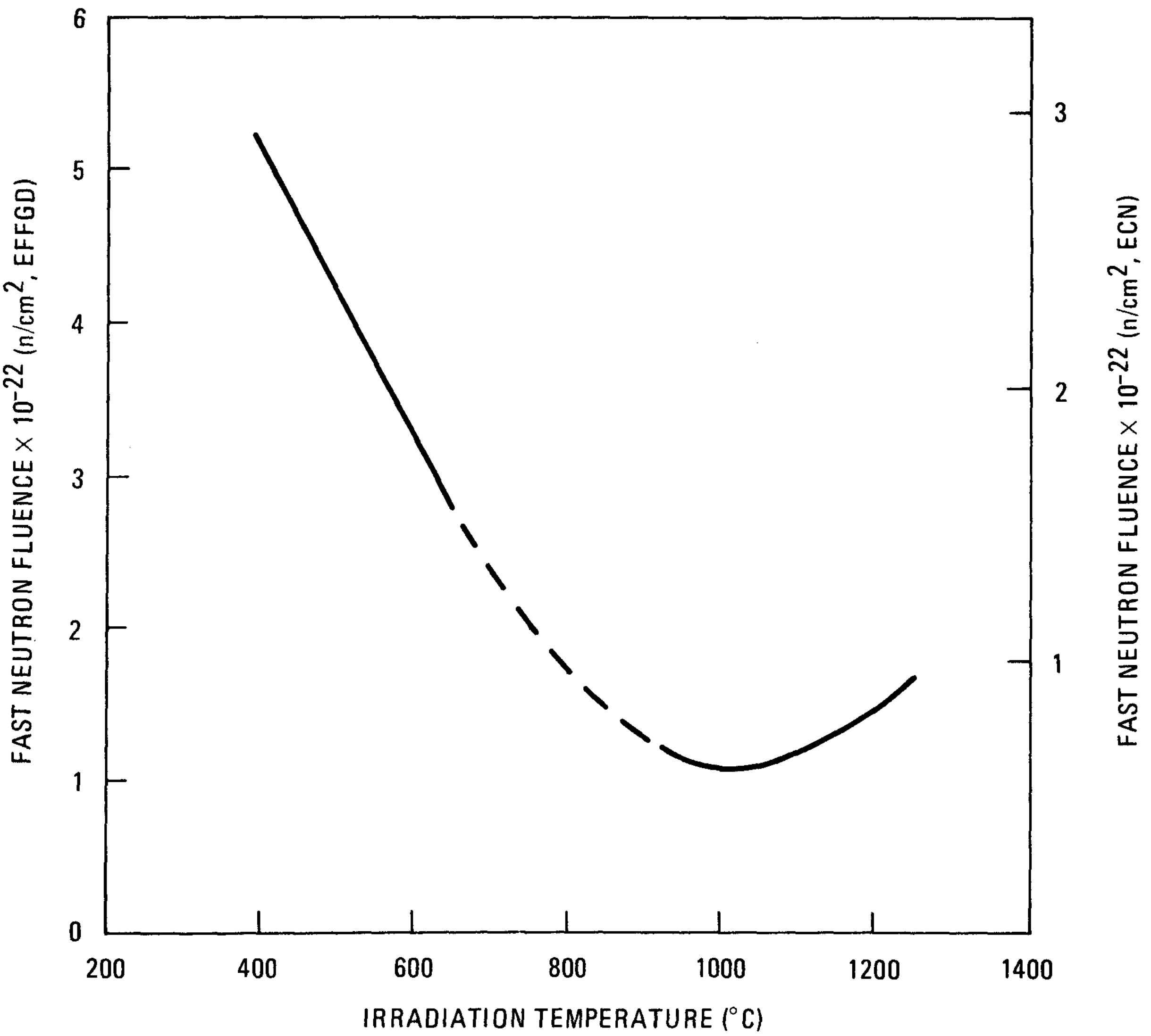

Fig. 2. Lifetime fluence of H-451 and similar graphites as a function of irradiation temperature

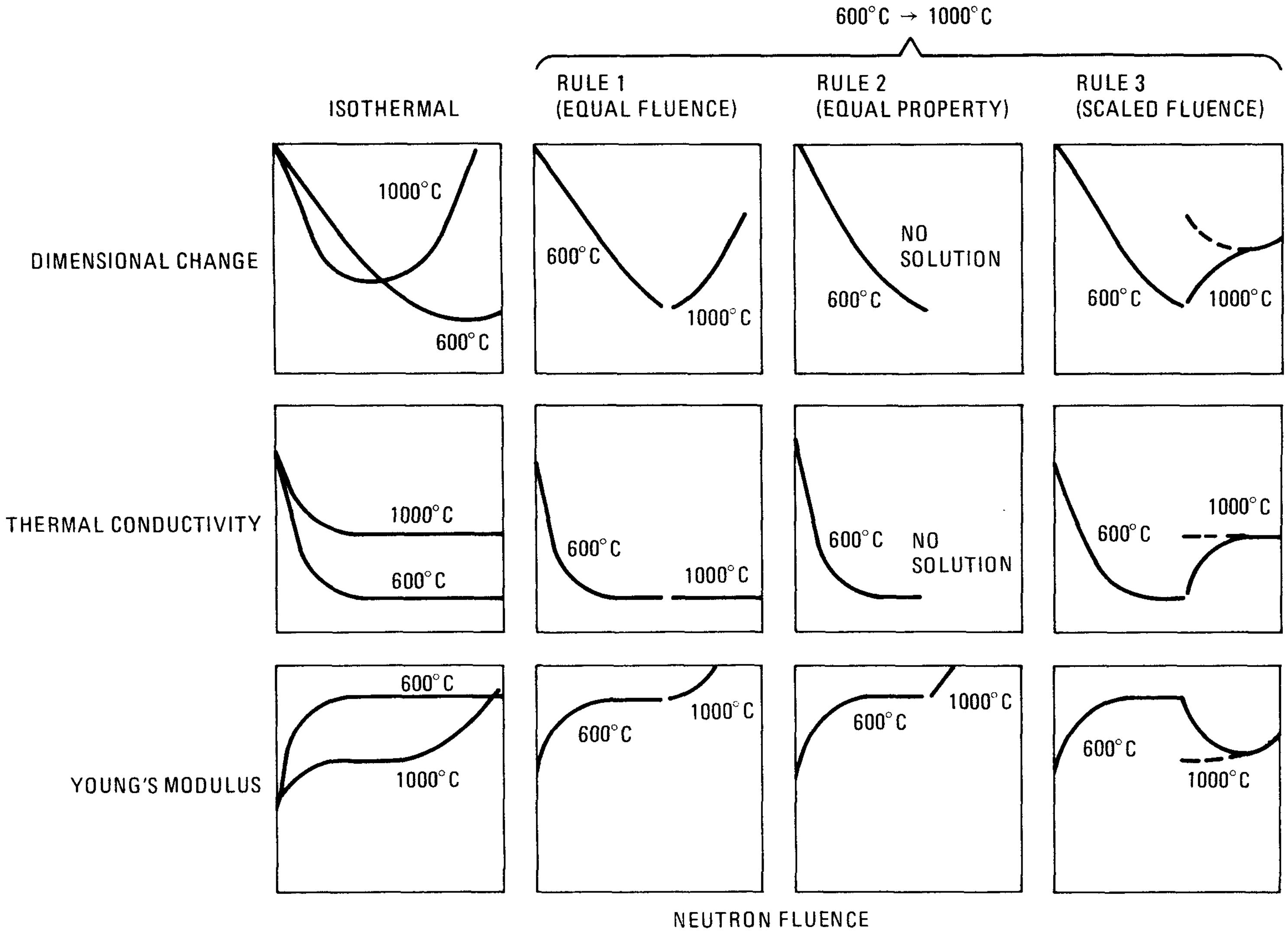

Fig. 3. Schematic illustration of the application of transposition rules to property changes in near-isotropic graphite: temperature increase

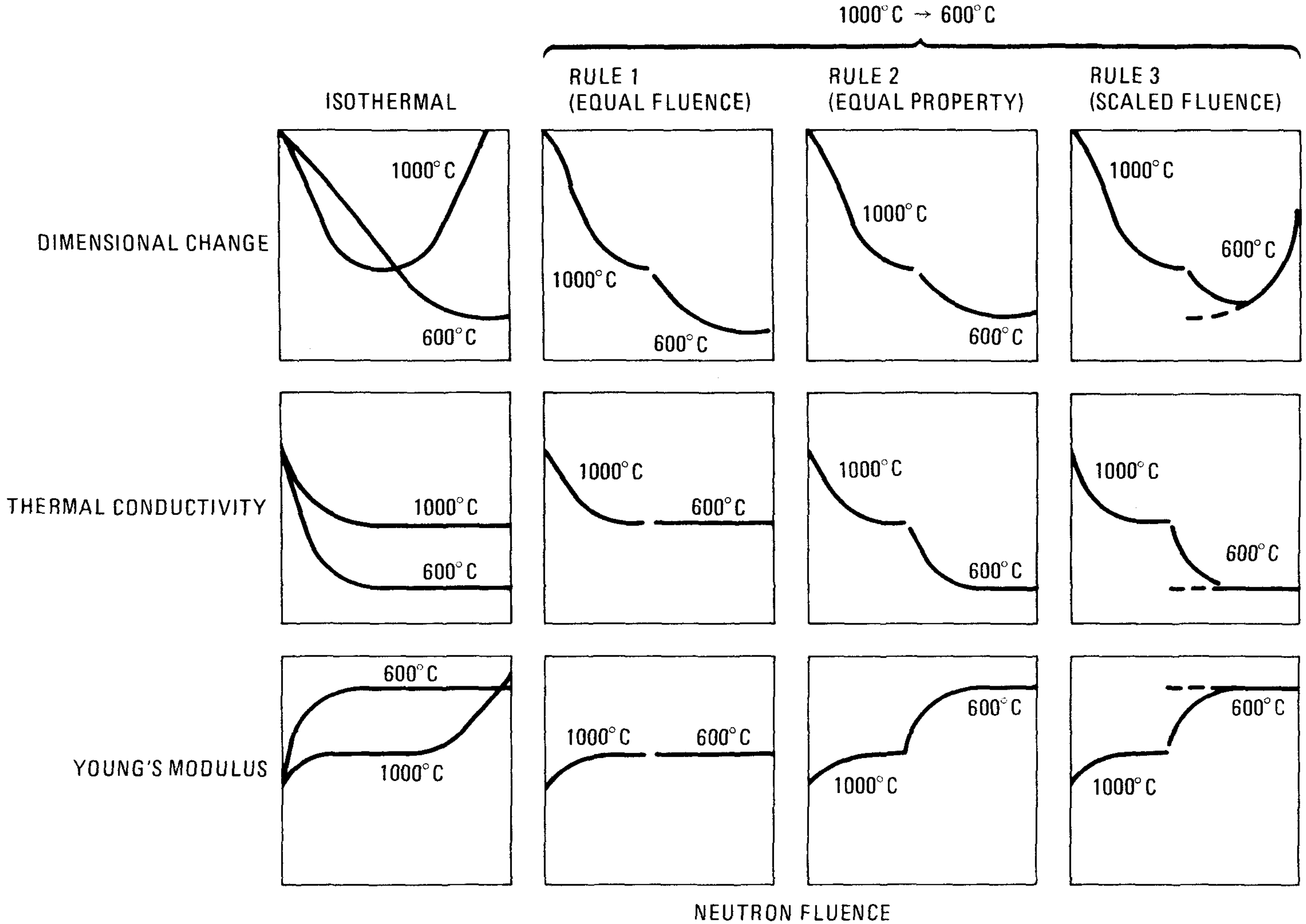

Fig. 4. Schematic illustration of the application of transposition rules to property changes in near-isotropic graphite: temperature decrease

4. EXPERIMENTAL DATA

4.1. DIMENSIONAL CHANGES

During irradiation tests on H-451 graphite at General Atomic Company (Ref. 2), several axial and radial specimens were interchanged between a high temperature cell and a low temperature cell, while companion specimens were irradiated isothermally. The temperatures were 650° to 700°C and 1030° to 1070°C, and both axial and radial specimens were used. Figure 5 shows the isothermal dimensional changes. Figure 6 shows the temperature change data for axial specimens. The dashed lines are predictions based on rule 3 (horizontal transposition at a scaled fluence). To make the transposition, the 650° to 700°C isotherm had to be extrapolated based on the known behavior of other graphites. Figure 7 shows similar data for the radial direction. The rule 3 transposition fits the data reasonably well. Rule 2 (horizontal transposition at equal dimensional change) would fit almost as well, whereas rule 1 (vertical transposition at equal fluence) would underpredict the changes following step-down.

An extensive series of tests were made at KFA on near-isotropic pitch coke graphite AS2-M-500 (Ref. 7). Specimens were shifted between irradiation cells with nominal temperatures of 400°, 600°, 700°C, and 1000°C. (Specimens shifted by 200°C or less are excluded from this review because data scatter masks the temperature change effects.) Figure 8 shows the isothermal dimensional changes in axial and radial specimens plotted as functions of neutron fluence. Figure 9 shows the results of step-up and step-down experiments on axial specimens and Figure 10 shows equivalent data for radial specimens. In Figs. 6, 7, 9, and 10, the dashed lines are the rule 3 predictions. Agreement between the data and the predicted behavior is reasonably good; however, extrapolation of the 410° to 450°C isotherm was necessary. Because the experiments were conducted in a region where the dimensional change curves are almost linear, any one of the three transposition rules would give similar predictions.

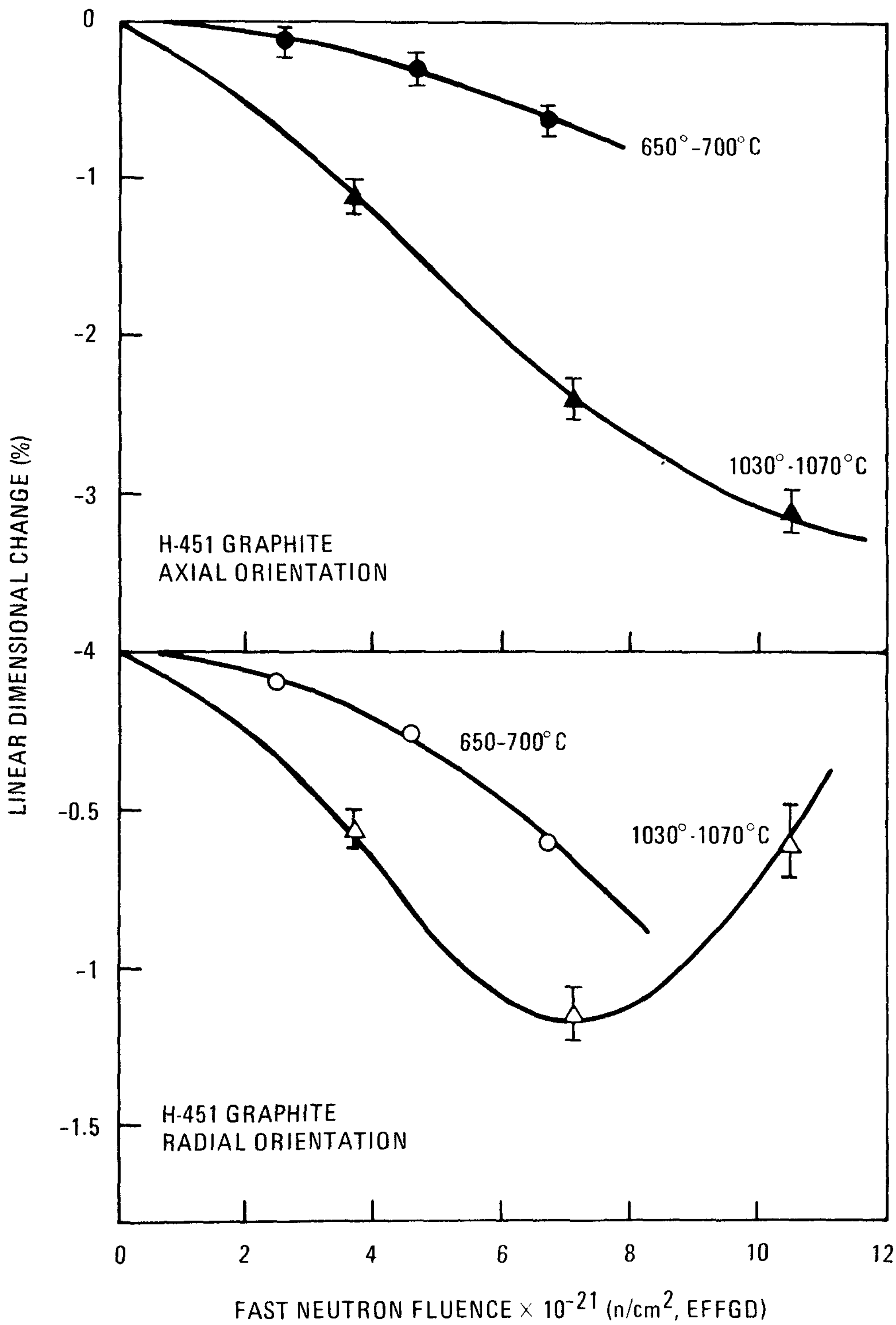

Fig. 5. Irradiation-induced dimensional changes in H-451 graphite: isothermal curves (data from Ref. 2)

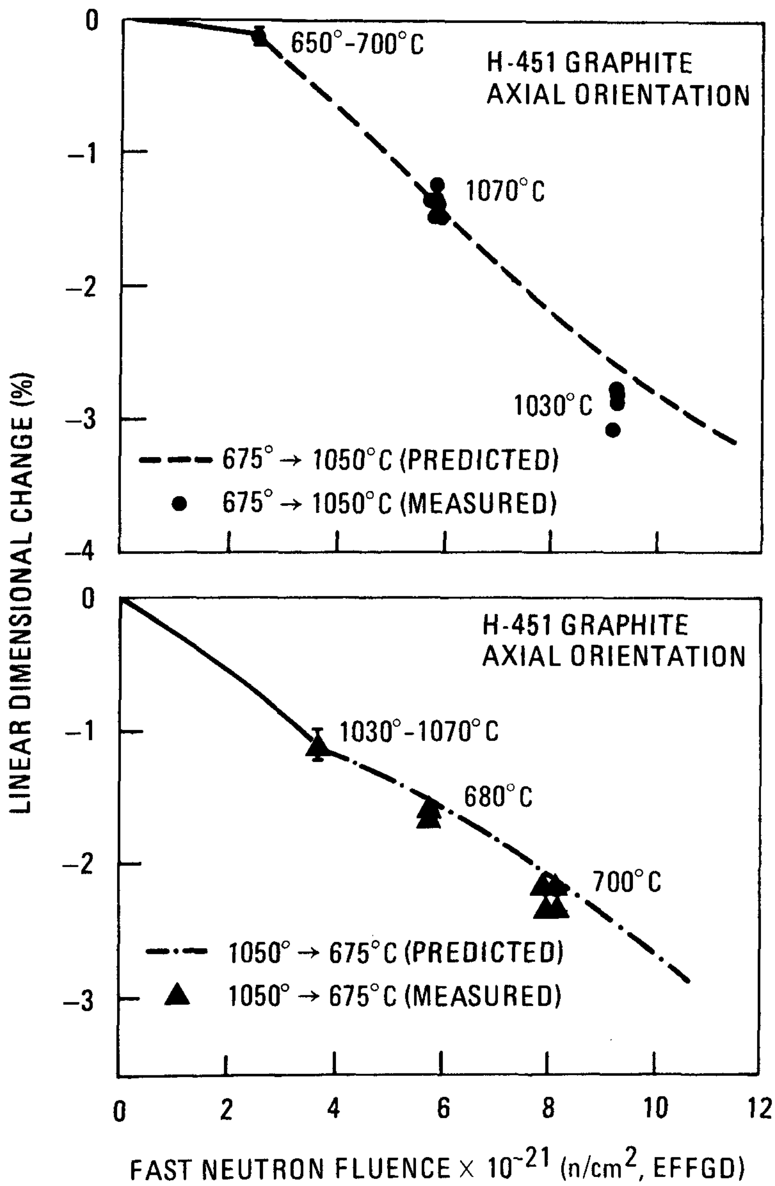

Fig. 6. Irradiation-induced dimensional changes in H-451 graphite: temperature change data, axial orientation (data from Ref. 2)

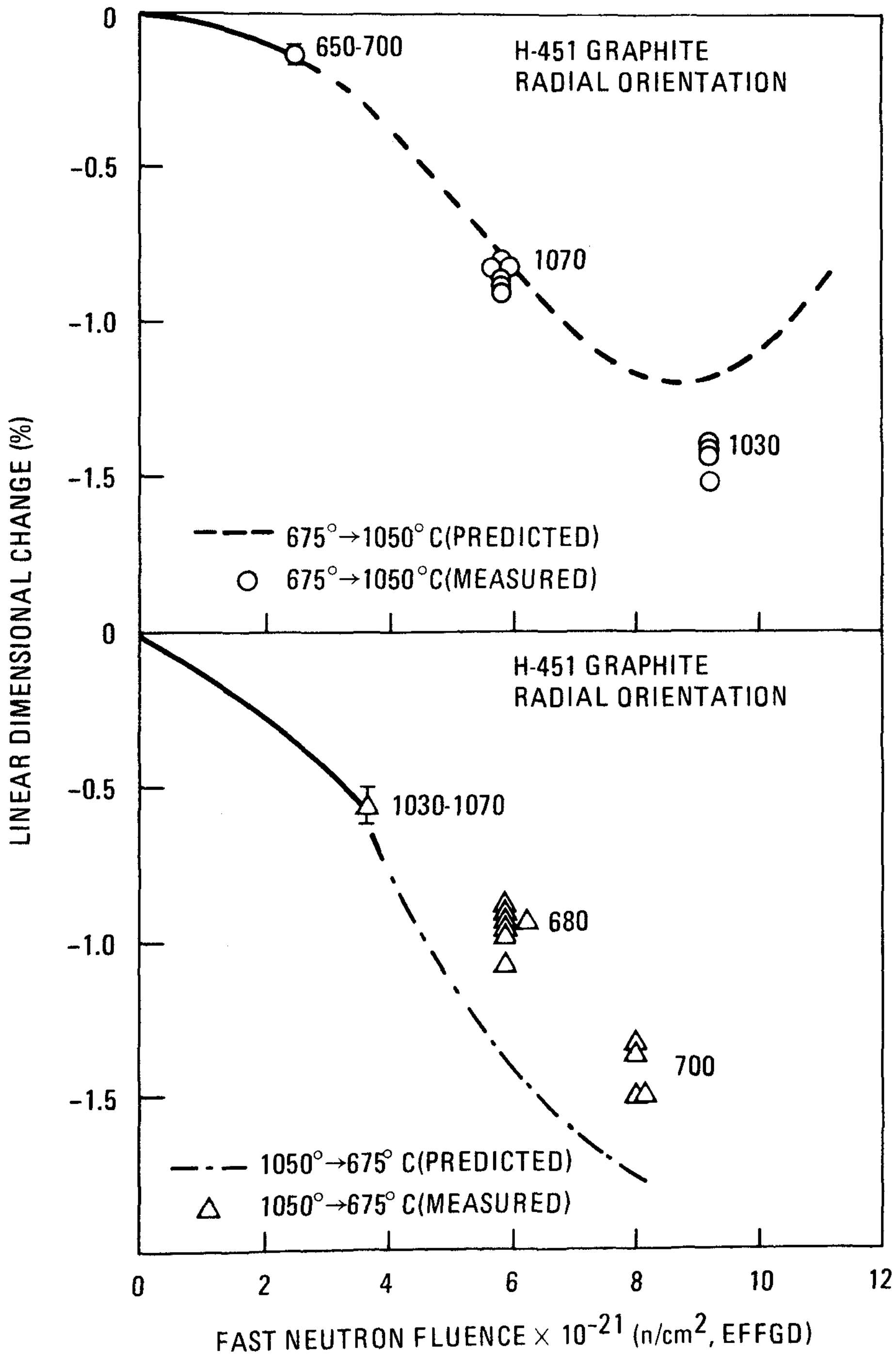

Fig. 7. Irradiation-induced dimensional changes in H-451 graphite: temperature change data, radial orientation (data from Ref. 2)

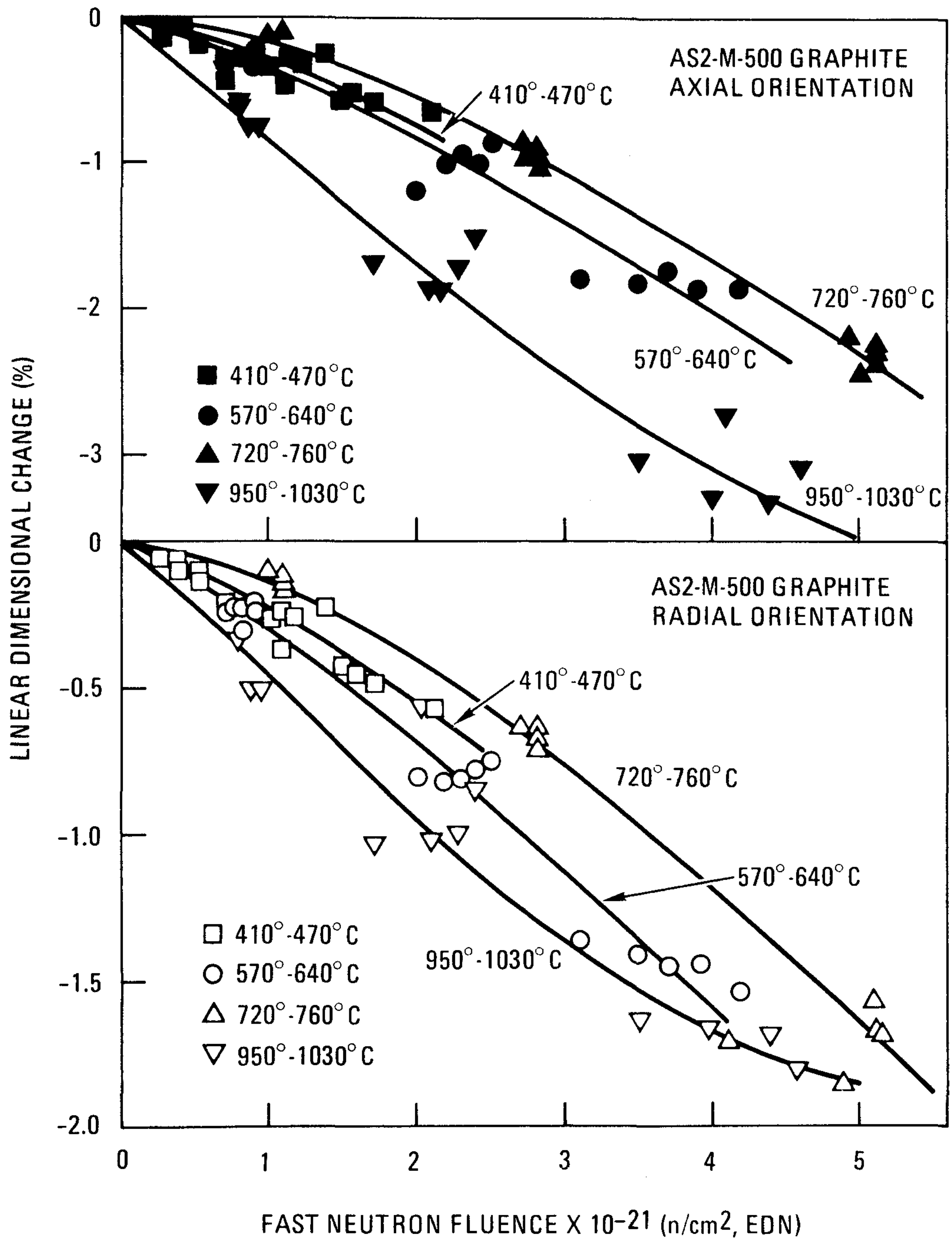

Fig. 8. Irradiation-induced dimensional changes in AS2-M-500 graphite: isothermal curves (data from Ref. 6)

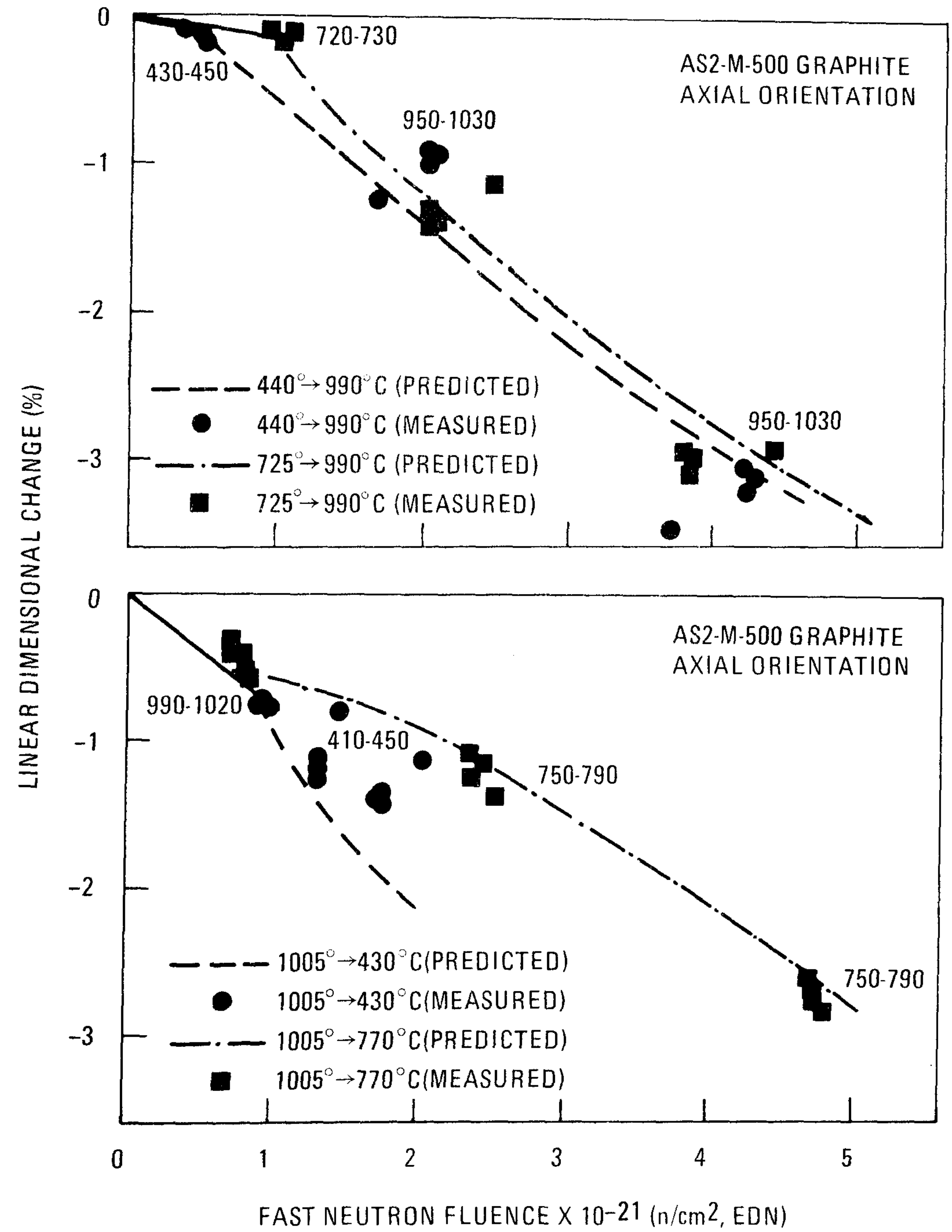

Fig. 9. Irradiation-induced dimensional changes in AS2-M-500 graphite: temperature change data, axial orientation (data from Ref. 7)

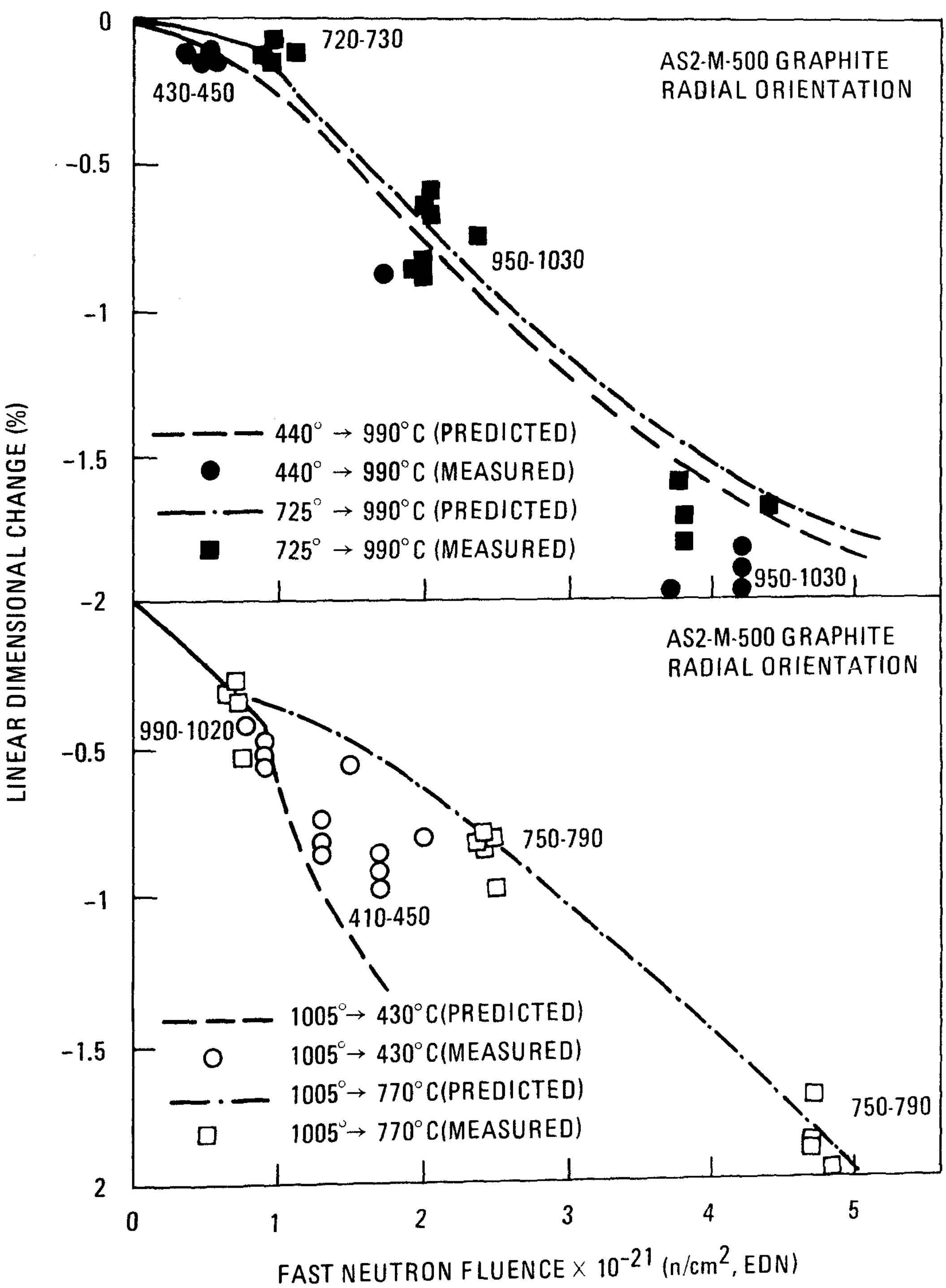

Fig. 10. Irradiation-induced dimensional changes in AS2-M-500 graphite: temperature change data, radial orientation (data from Ref. 6)

A third set of temperature change data on gilsocarbon-based graphite (Dragon grade 95) and semi-isostatically pressed graphite matrix material was published by Delle, et al. (Ref. 4). In these experiments, the irradiations were taken almost to the point of minimum dimensional change. Isothermal curves for the grade 95 graphite are shown in Fig. 11 and the results of the temperature change experiments are shown in Fig. 12. Similar data for the matrix material appear in Figs. 13 and 14. The rule 3 predictions fit the observations fairly well, with the exception of the graphite specimens whose temperature was shifted from 900°C to 1200°C (Fig. 12). Although rules 2 and 3 predict continued shrinkage, expansion was actually observed. In the rest of the cases (for example, the 1200°C → 800°C shift in the graphite specimens, and the 900°C → 1300°C shift in the matrix specimens), rule 3 transposition matches the data better than either rules 1 or 2.

4.2. YOUNG'S MODULUS

Reference 6 contains data obtained by KFA on the effects of systematic changes in irradiation temperature on the dynamic Young's modulus of AS2-M-500 graphite. Isothermal data are shown in Fig. 15, and data for the percent change in Young's modulus for temperature changes exceeding 200°C are shown in Fig. 16. The data are in very good agreement with rule 3 predictions, whereas rules 1 or 2 do not fit the observations.

4.3. THERMAL CONDUCTIVITY

During irradiation experiments by General Atomic Company (Ref. 2) some specimens of H-451 graphite were interchanged between irradiation temperatures of 1350°C and 600° to 650°C. The thermal conductivity of the irradiated specimens was measured at room temperature. Isothermal irradiation results are shown in Fig. 17 and temperature shift data are shown in Fig. 18. The observations agree very well with rule 3 predictions. In contrast, rule 1 would predict no change in conductivity after the temperature change and rule 2 would give no solution in the temperature rise case.

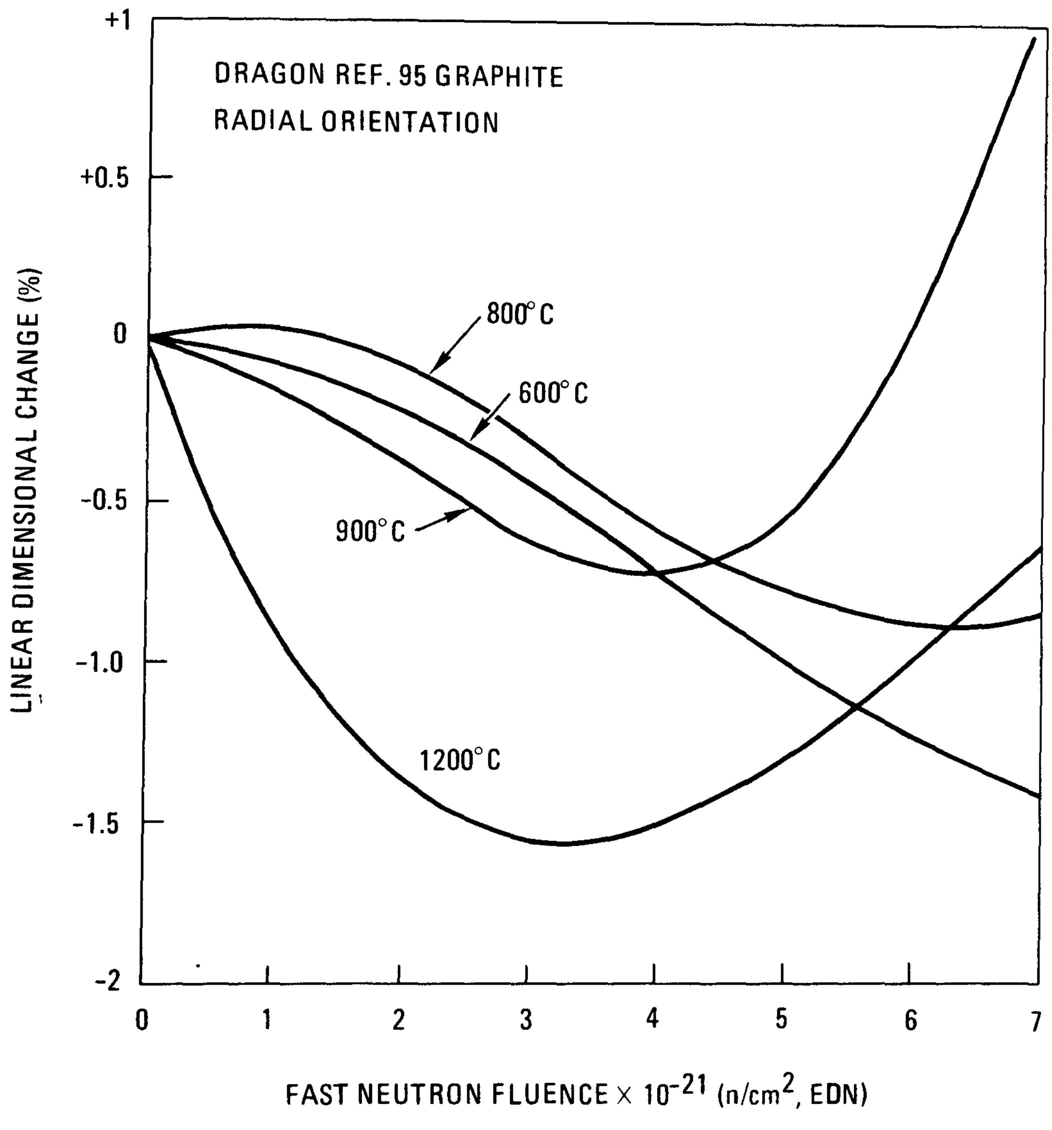

Fig. 11. Irradiation-induced dimensional changes in Dragon grade 95 graphite: isothermal changes (data from Ref. 4)

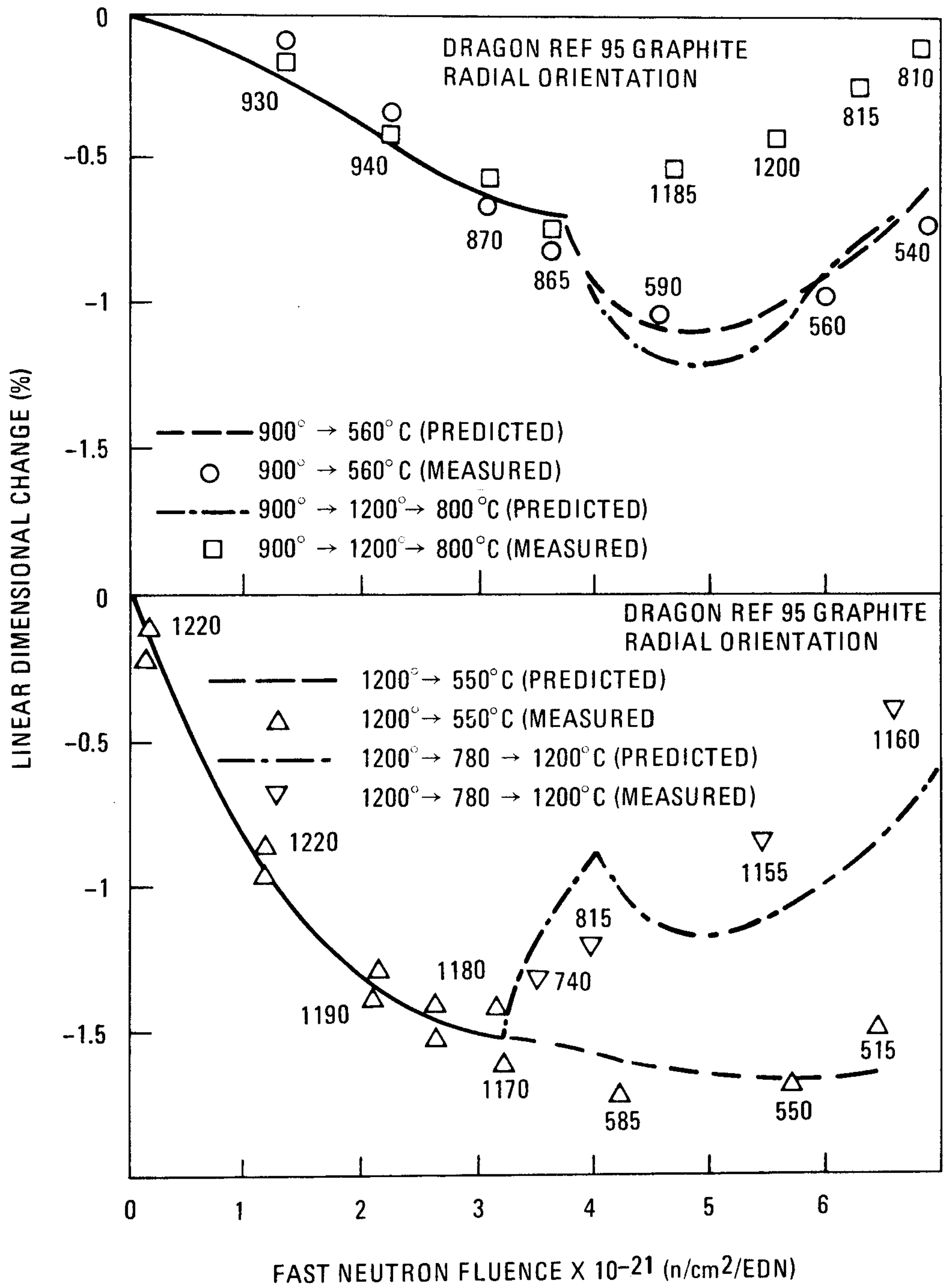

Fig. 12. Irradiation-induced dimensional changes in Dragon grade 95 graphite: temperature change data (data from Ref. 4)

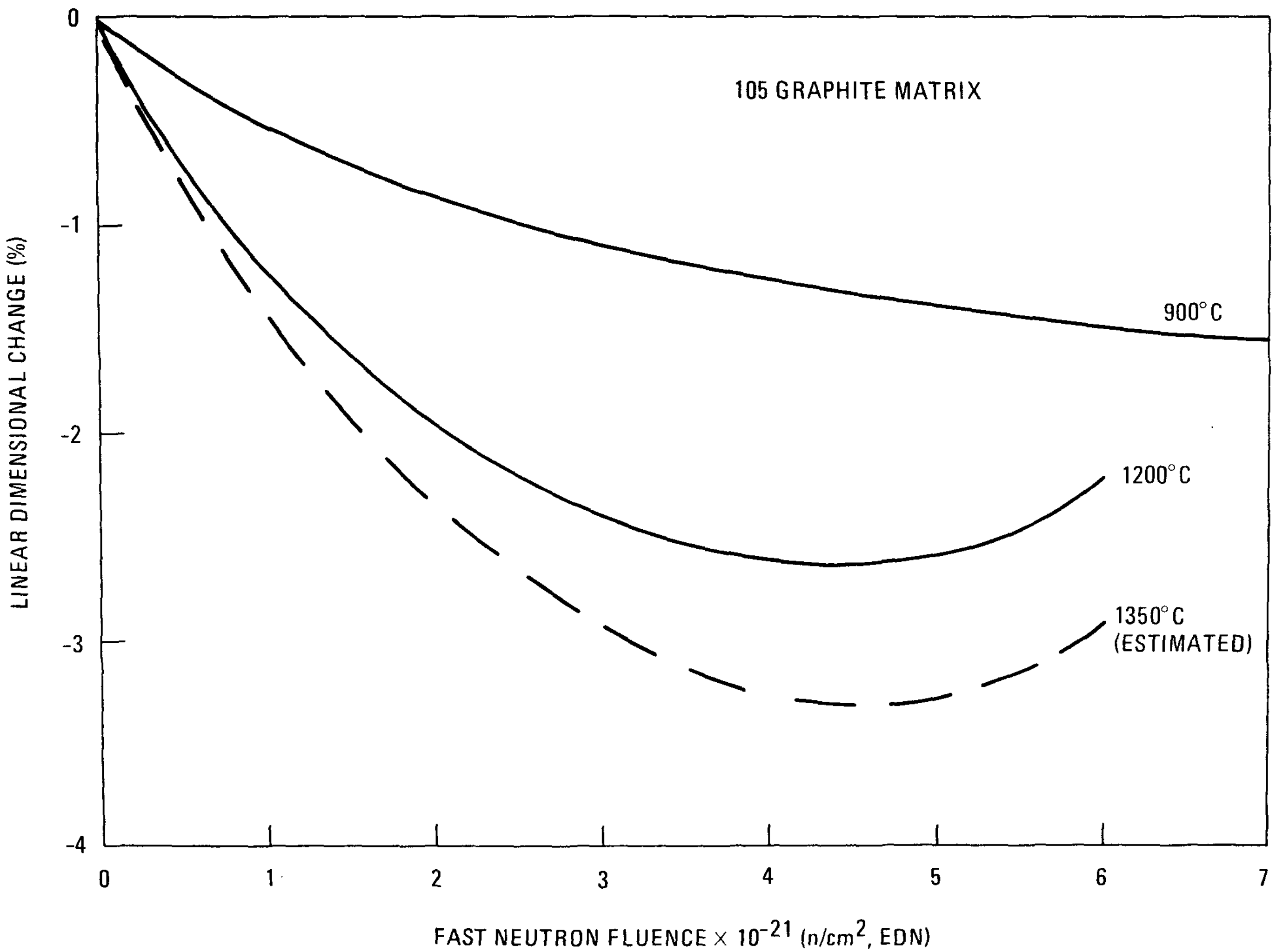

Fig. 13. Irradiation-induced dimensional changes in semi-isostatically pressed graphite matrix material: isothermal changes (data from Ref. 4)

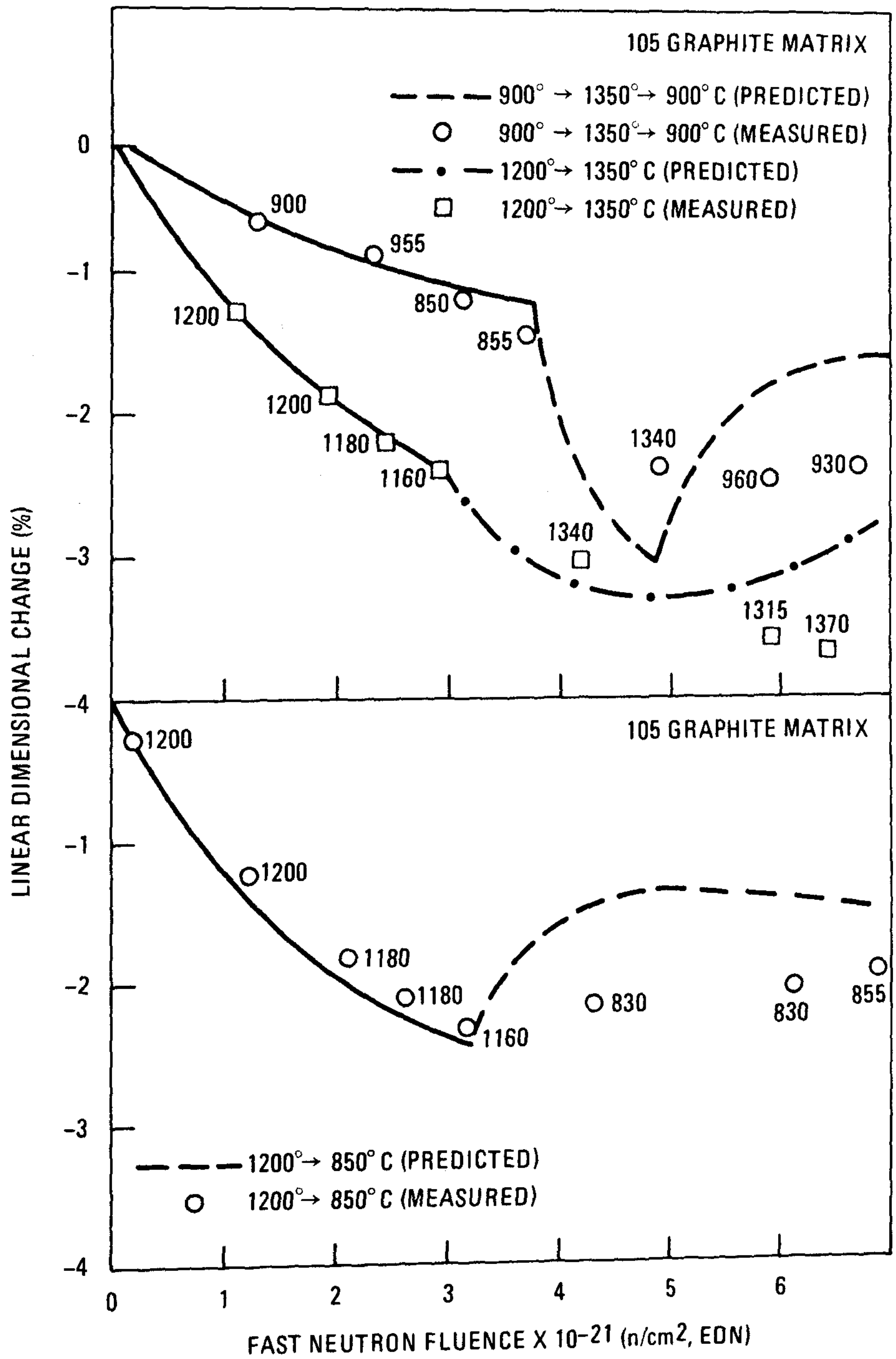

Fig. 14. Irradiation-induced dimensional changes in semi-isostatically pressed graphite matrix material: temperature change data (data from Ref. 4)

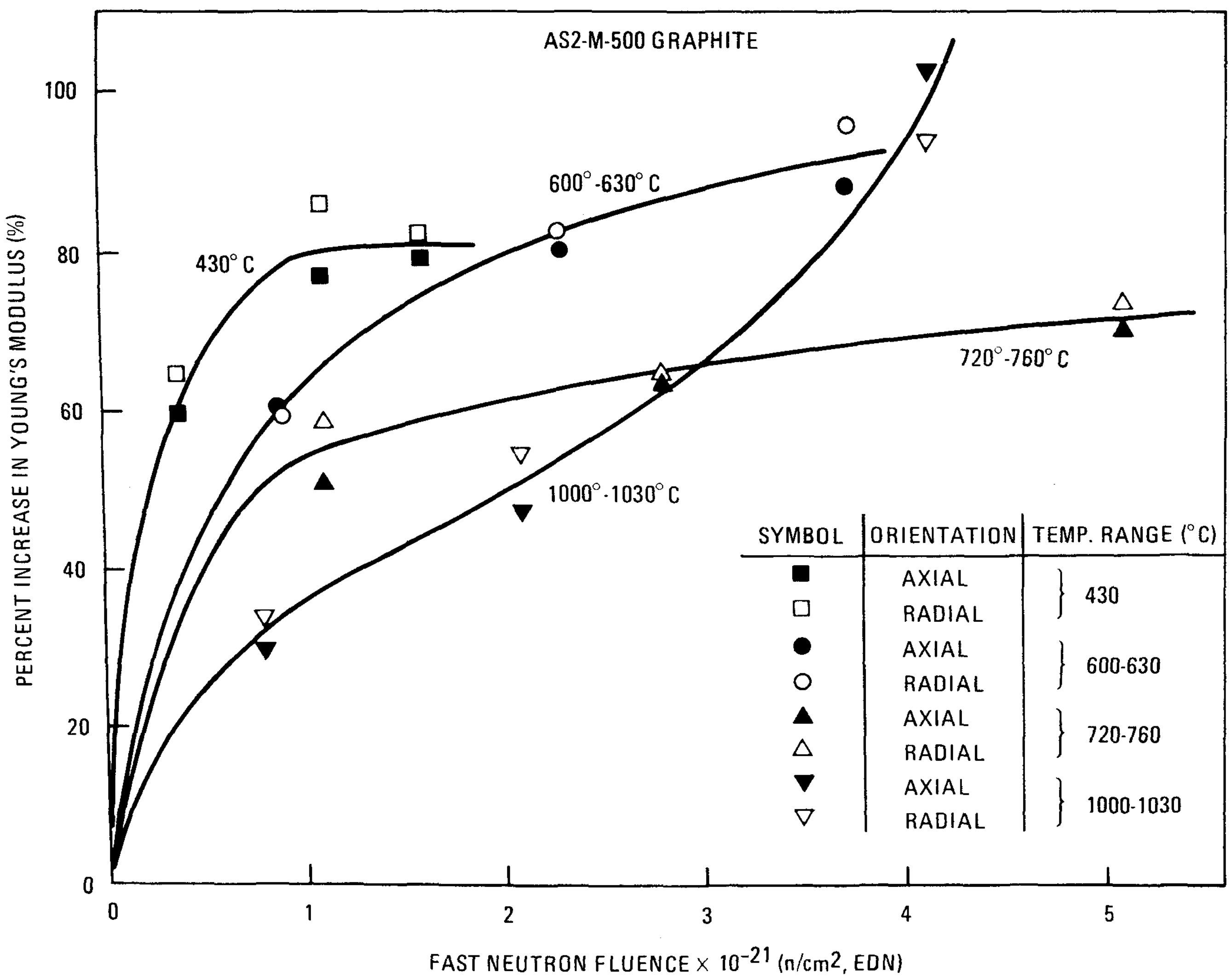

Fig. 15. Irradiation-induced changes in Young's modulus of AS2-M-500 graphite: isothermal changes (data from Ref.7)

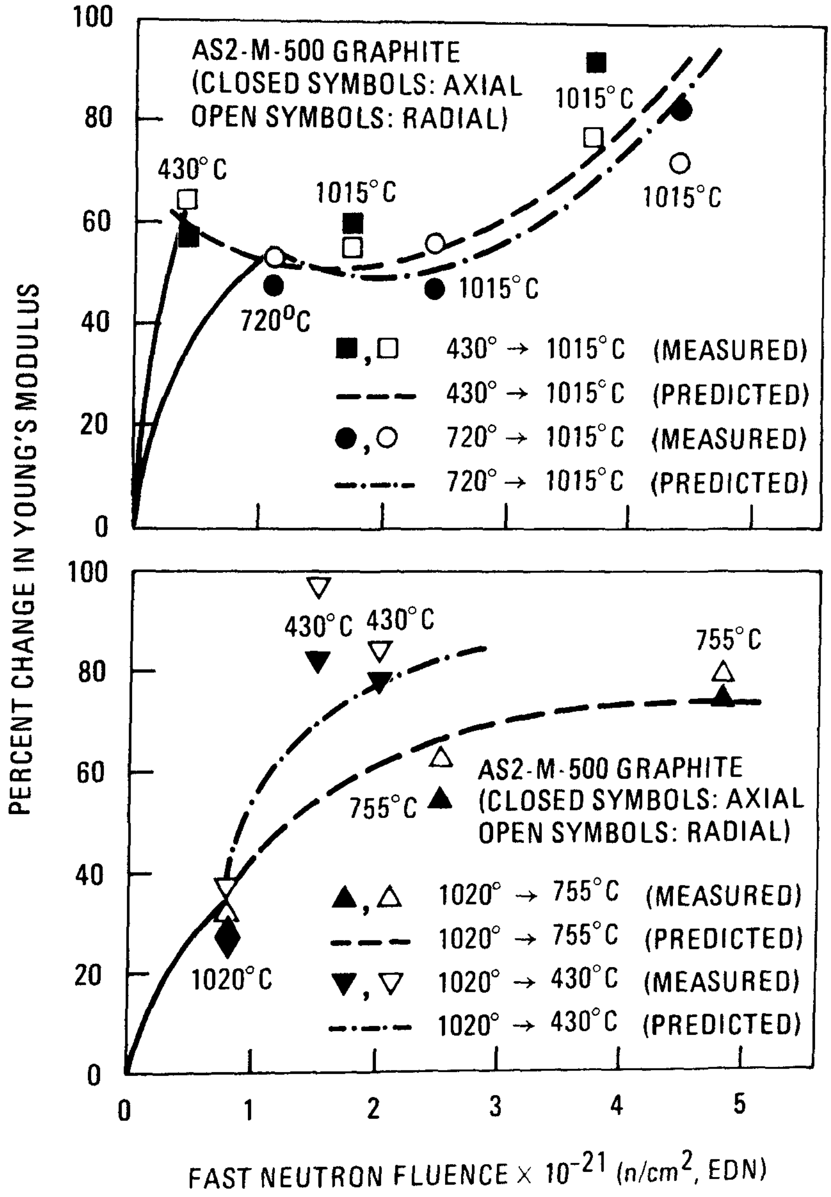

Fig. 16. Irradiation-induced changes in Young's modulus of AS2-M-500 graphite: temperature change data (data from Ref. 7)

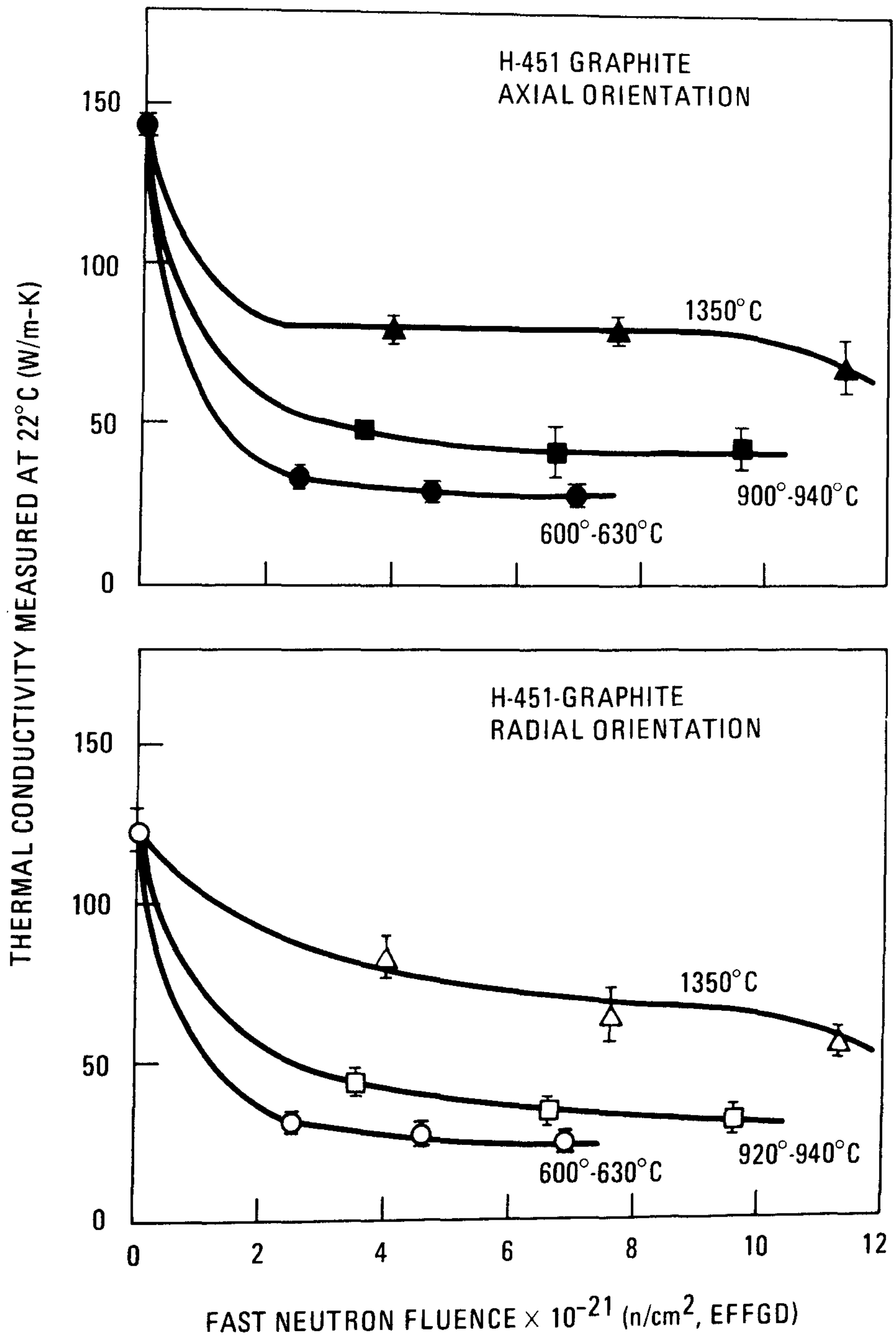

Fig. 17. Irradiation-induced changes in the room temperature thermal conductivity of H-451 graphite: isothermal curves (data from Ref. 2)

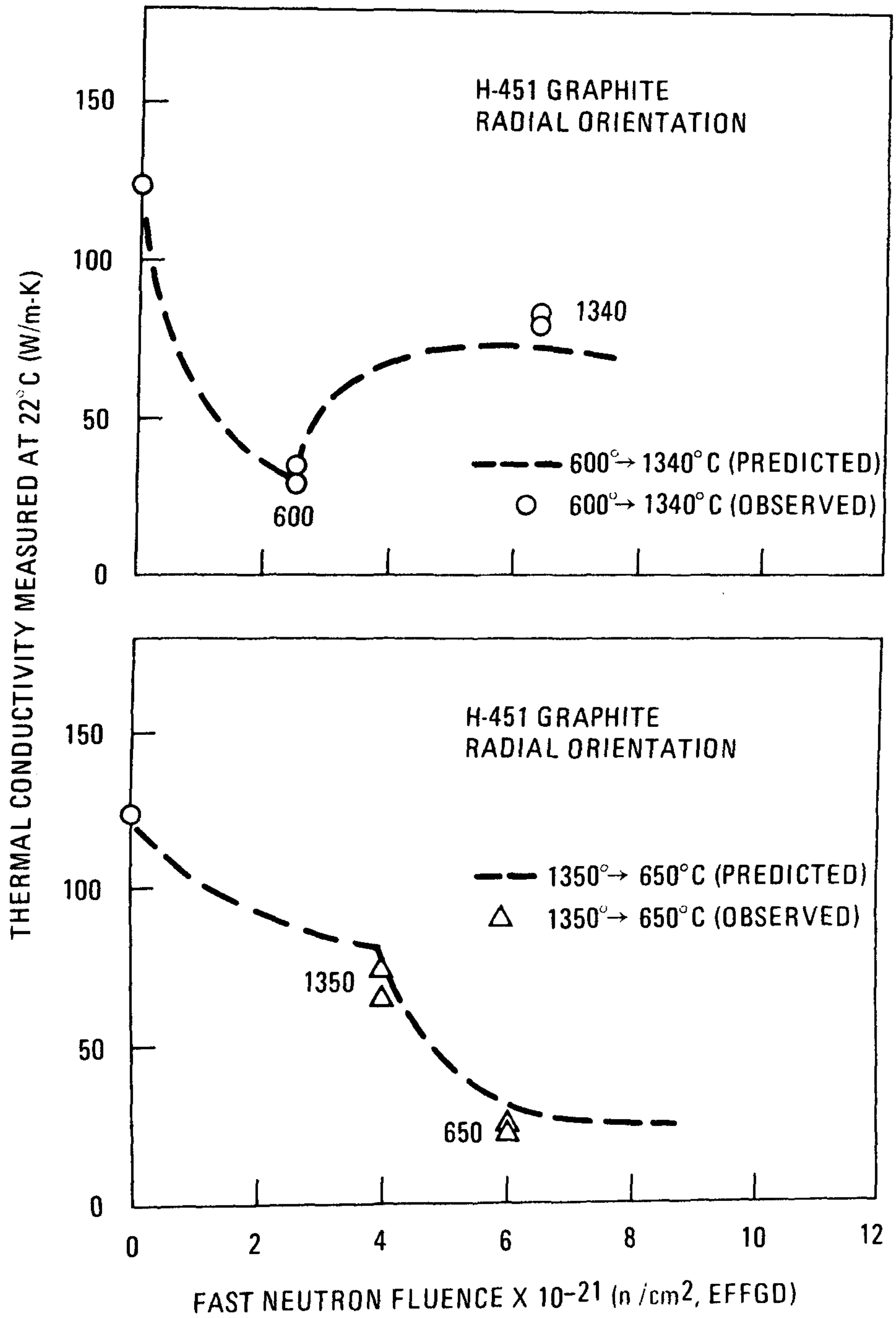

Fig. 18. Irradiation-induced changes in the room temperature thermal conductivity of H-451 graphite: temperature change data (data from Ref. 2)

4.4. THERMAL EXPANSIVITY

During the KFA experiments (Ref. 7), the thermal conductivity of some AS2-M-500 specimens was measured. The isothermal data are plotted in Fig. 19, and the temperature change data in Figs. 20 and 21. Again, rule 3 transposition shows fairly good overall agreement with the data. However, rule 1 transposition fails to predict the rise in thermal expansivity when the irradiation temperature is dropped from 1020° to 430°C, and rule 2 transposition is impossible in some cases.

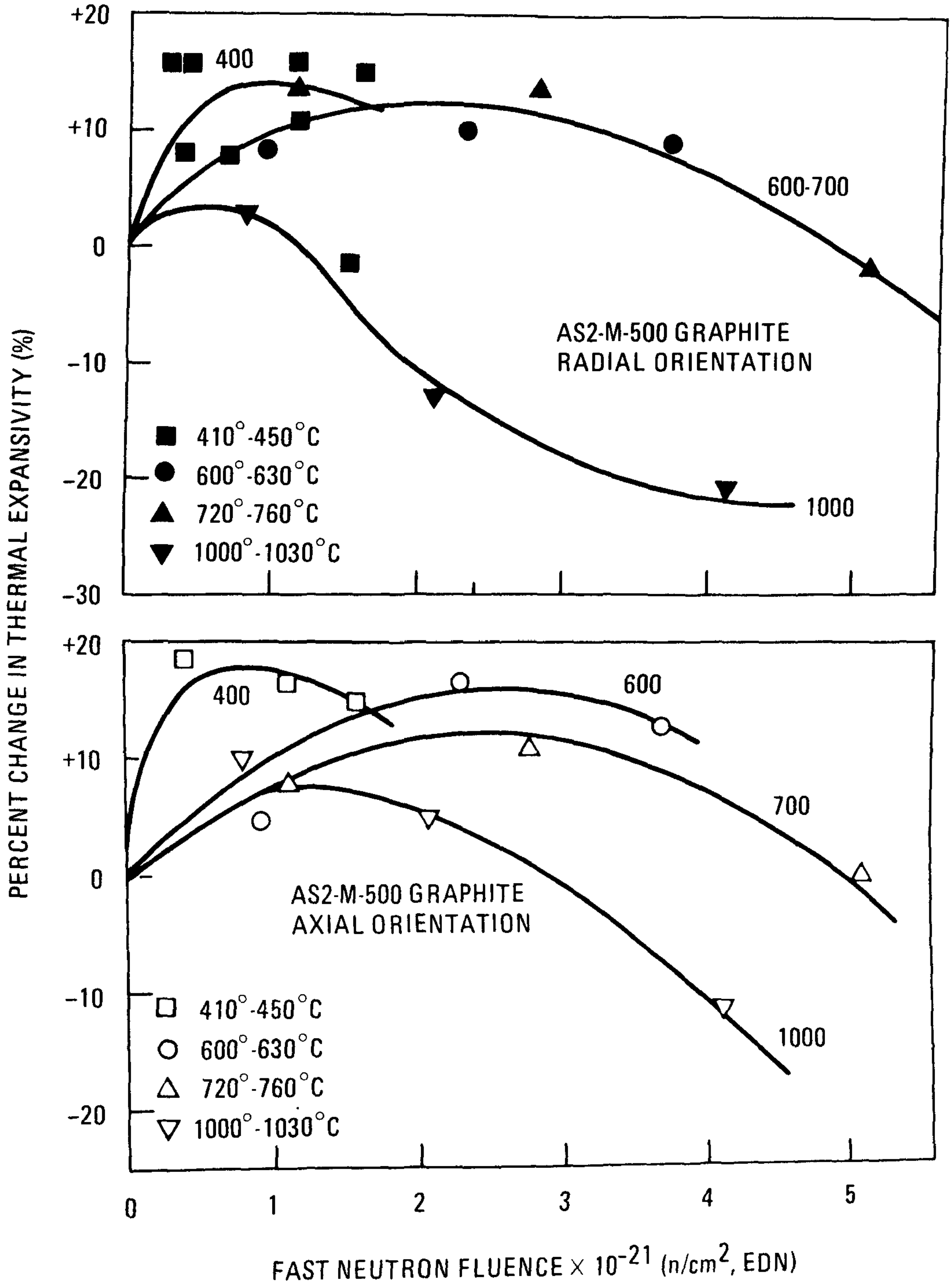

Fig. 19. Irradiation-induced changes in the thermal expansivity of AS2-M-500 graphite: isothermal curves (data from Ref. 7)

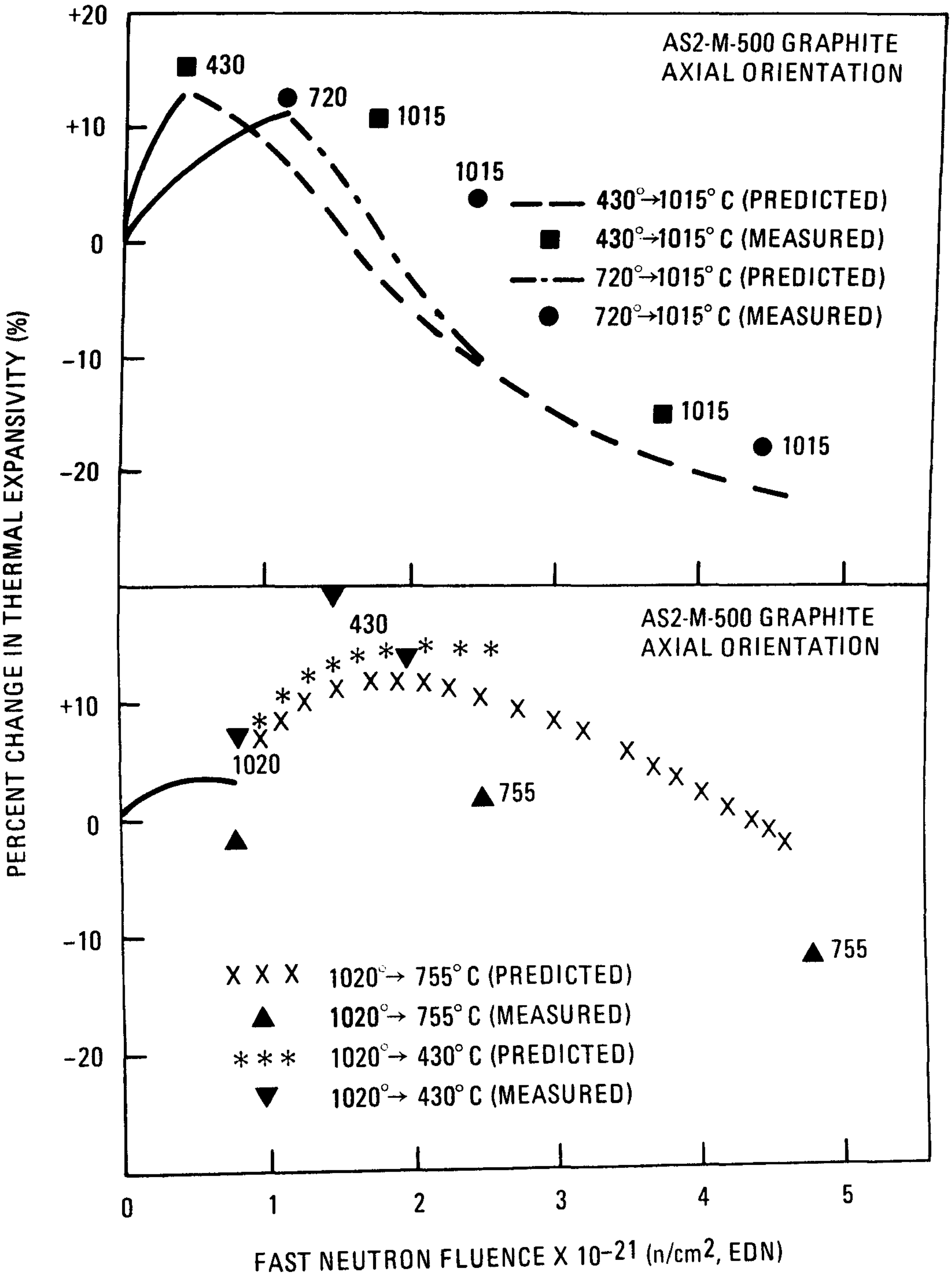

Fig. 20. Irradiation-induced changes in the thermal conductivity of AS2-M-500 graphite: temperature change data, axial orientation (data from Ref. 7)

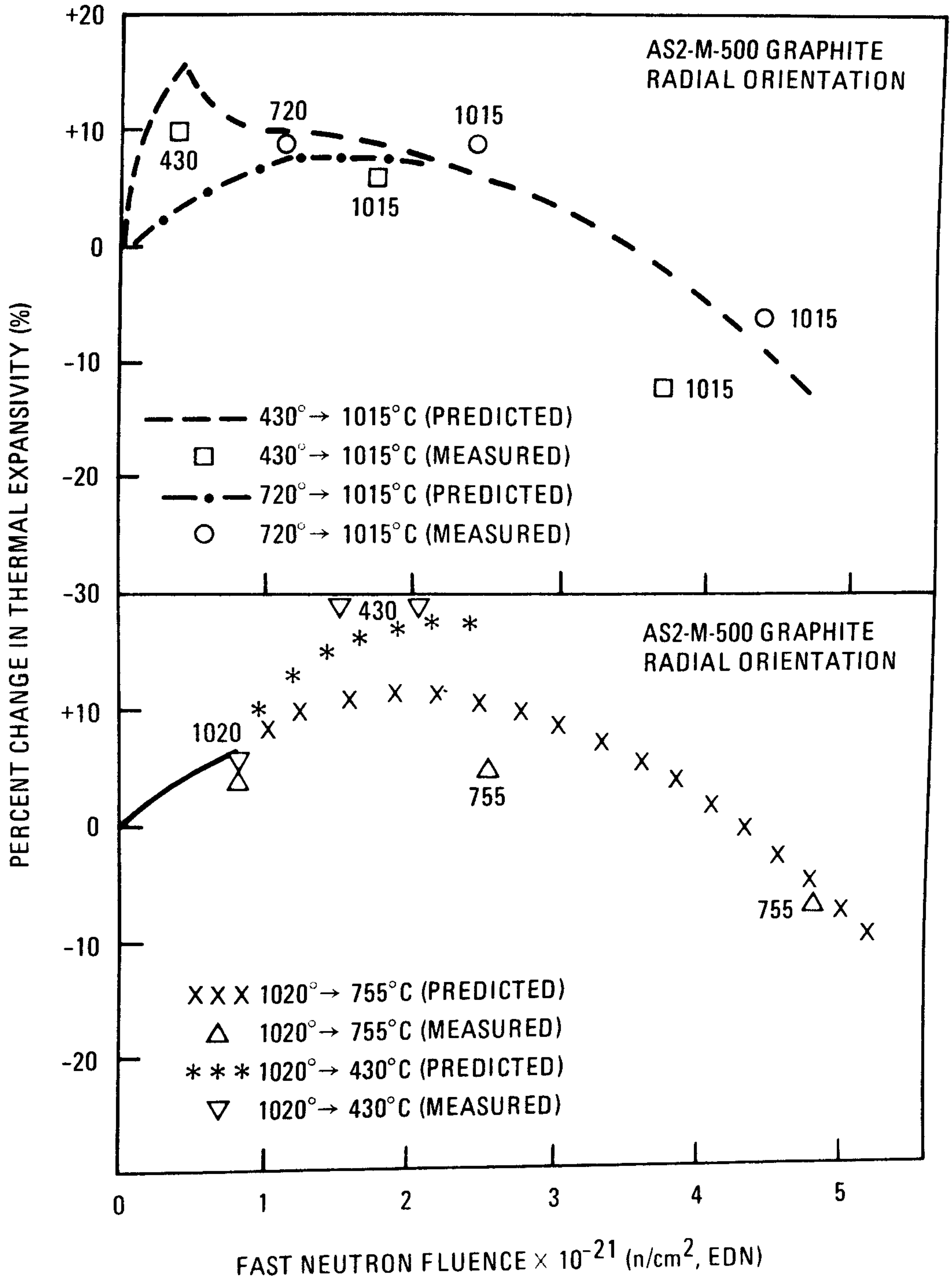

Fig. 21. Irradiation-induced changes in the thermal expansivity of AS2-M-500 graphite: temperature change data, radial orientation (data from Ref. 7)

5. SUMMARY AND CONCLUSIONS

Routine irradiation tests on graphite are carried out at constant temperature and the resulting design data are presented in the form of families of isothermal plots showing the change in property as a function of fast neutron fluence. When service conditions require the irradiation temperature to change, design calculations must use combinations of isothermal plots to predict the graphite properties. In the present report three alternative rules for transposing isothermal curves are discussed.

Rule 1: Vertical transposition at equal fluence [Fig. 1(B)]: this procedure is simple, but fails to predict the changes in properties such as thermal conductivity which are controlled by a transient population of small defect clusters.

Rule 2: Horizontal transposition at equal property value [Fig. 1(C)]: this procedure has some justification, but frequently fails to provide a solution.

Rule 3: Horizontal transposition at scaled fluence [Fig. 1(D)]: this procedure provides a physically realistic method which always yields a solution and can be used for transient property changes such as Young's modulus and thermal conductivity.

Experimental data from several programs in which the irradiation temperature of graphite specimens was systematically changed were reviewed. Measurements of changes in dimensions, Young's modulus thermal conductivity, and thermal expansivity are plotted in Figs. 5 through 21.

Overall, the measurements agree well with predictions based on the third transposition rule, whereas the first and second rules sometimes give rise to false predictions or no predictions at all.

The suggested procedure for combining isotherms by horizontal transposition at a scaled fluence is as follows. The fluence accumulated at any irradiation temperature, T, is converted to a scaled fluence by dividing by the lifetime fluence, L(T). L(T) is taken to be the fluence where the dimensional change becomes positive and it is given for H-451 and similar graphites in Fig. 2.

If a specimen changes temperature from T_1 to T_2 after accumulating a certain scaled fluence the T_2 isotherm is transposed horizontally to the same scaled fluence [Fig. 1(D)]. Any gap between the two isotherms is progressively reduced according to the expression:

$$y = y^* + \Delta\dot{y} \exp\left(-\frac{\gamma}{\tau}\right) , \qquad (2)$$

where y is the predicted property value, y* is the property value on the transposed T_2 isotherm, Δy is the gap between the isotherms at the temperature change point, γ is the fluence measured from the temperature change point, and τ is a time constant whose value is taken to be 1×10^{21} n/cm^2 (equivalent fission fluence for graphite damage).

ACKNOWLEDGEMENTS

General Atomic's contribution to this work was supported by Contract DE-AT03-76ET-35300 for the San Francisco office of the Department of Energy. The contribution from the Federal Republic of Germany was carried out in the framework of the Project "Hochtemperaturreaktor-Brennstoffkreislauf" (High Temperature Reactor Fuel Cycle) that includes the partners Gelsenberg AG, Gesellschaft fuer Hochtemperaturreaktor-Technik GmbH, Hochtemperaturreaktor-Brennelement GmbH, Sigri Elektrographit GmbH, Rindsdorff-Werke GmbH and is financed by BMFT (Federal Ministry for Research and Tecnnology) and the State of Nordrhein-Westfalen.

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